

CHEMICAL MODIFICATION AND CHARACTERIZATION OF KENAF FIBER

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ABSTRACT

Composites produced by natural fiber as a reinforcement material were environmentally friendly since natural fiber can be biodegradable but it has some limitation because of their surface impurities. In this study, alkali treatment was performed on kenaf bast fibers in order to remove surface impurities. Grinding and without grinding kenaf bast fibers has been used. Kenaf bast fibers were immersed into 3%, 6%, and 9% concentrated sodium hydroxide (NaOH) solutions for 1 h, 3 h and 6 h. The effects of solution concentrations and treatment times on the mechanical properties of kenaf bast fibers were evaluated. Kappa test was achieved by using titration process and Scanning Electron Microscope (SEM) analysis of untreated and alkali treated kenaf bast fibers were carried out. Those results for Kappa test showed that the kenaf bast fibers treated with 6% NaOH at 3 h has lower kappa number and it showed that the lignin content was lower as well. Besides, results of scanning electron microscope analysis showed that the surface of fiber became cleaner after alkali treatment. In addition, composites reinforced by untreated and alkali-treated kenaf bast fibers were fabricated by using hot press method. Tensile tests were carried out for produced composites. Results showed that tensile strength of the composite using treated and without grinding fibers increased in comparison with the composite using without grinding untreated fibers and grinding and without grinding fibers.

ABSTRAK

Komposit yang dihasilkan daripada fiber semulajadi tidak akan menyebabkan pencemaran alam sekitar memandangkan fiber semulajadi mudah untuk dilupuskan. Rawatan menggunakan larutan alkali telah dilakukan ke atas kenaf fiber untuk tujuan mengubah struktur permukaan kenaf fiber. Dalam projek ini juga, terdapat dua jenis kenaf fiber yang telah digunakan iaitu kenaf fiber yang panjang dan kenaf fiber yang telah dihancurkan. Rawatan ini telah dijalankan dengan merendam kenaf fiber di dalam larutan natrium hidroksid (NaOH) dengan kepekatan yang berbeza iaitu 3%, 6%, dan 9% untuk masa yang berlainan iaitu 1 jam, 3 jam dan 6 jam. Kesan kepekatan dan masa yang berbeza ke atas kenaf fiber telah dinilai. Ujian Kappa dilakukan dengan menggunakan kaedah 'titration' dan 'Scanning Electron Microscope' ataupun SEM analisis juga turut dijalankan. Berdasarkan semua keputusan untuk ujian Kappa, kenaf fiber yang dirawat dengan menggunakan 6% NaOH untuk masa 3 jam mempunyai nilai kappa yang lebih rendah. Selain itu, keputusan untuk SEM pula menunjukkan permukaan kenaf fiber yang dirawat dengan larutan alkali lebih licin berbanding dengan permukaan kenaf fiber yang tidak dirawat. Kemudian komposit telah dihasilkan dengan menggunakan kenaf fiber yang dirawat dan telah dirawat sebagai penyokong melalui alat yang dikenali sebagai 'hot press'. Ujian kekuatan keatas komposit yang terhasil telah dijalankan. Keputusan untuk ujian tersebut menunjukkan komposit yang dihasilkan dengan menggunakan kenaf fiber yang panjang dan dirawat mempunyai kekuatan yang lebih besar.

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LIST OF ABBREVIATIONS

NaOH	Natrium hydroxide
NaOCl	Sodium hypochlorite
H ₂ O ₂	Hydrogen peroxide
OCI ⁻	Hypochlorite ion
Na ⁺	Sodium ion
AOX	Adsorbable organically bond halogens
HOO ⁻	Perhydroxyl anion
SEM	Scanning Electron Microscope
BSE	Backscattered electrons
DBSE	Diffacted backscattered electrons
KFI	Kenaf Fiber Industry
CH ₃ COOH	Acetic acid

KI

Potassium iodide

 H_2SO_4

Sulphuric acid

 KMnO_4

Potassium permanganate

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CHAPTER 1

INTRODUCTION

1.1 Background of The Study

The growing global environmental concern, high rate of depletion of petroleum resources, as well as new environmental regulations have forced the search for new fiber reinforced composite materials that are compatible with the environment (Gaceva, Dekanski, Panic, Poleti, Grodanov, Buzarovska, Aavella, and Gentile, 2006). The classical composite materials manufactured with fiberglass as reinforcement present environmental problems at the end of their useful life. The alternative could be the use of vegetables fibers as reinforcement (Corrales, Llop, Mutjie, Vilaseca, and Gandini, 2002). Natural fibers represent environmentally friendly alternatives to conventional reinforcing fibers, due to the following advantages: they are abundantly available renewable resources; they are nontoxic; natural fibers used in polymer composites can lead to materials with high specific strength because of their low density (Gaceva, et al., 2006).

On the contrary, the major limitations of using these fibers as reinforcements in such matrices include poor interfacial bonding between hydrophilic natural fibers and hydrophobic polymer matrix (Gaceva, et al., 2006) and the high moisture absorption, which could result in dimensional changes of the fibers that may

lead to micro-cracking of the composite and degradation of mechanical properties (Mohd Edeerozey, Akil, Azhar and Zainal Ariffin, 2006) due to the degradation of cellulose of the fibers (Corrales, et al, 2002). All of these drawbacks are caused by the surface impurities of the fiber. Thus, fiber surface modification methods have been developed to modify the surface fiber because mechanical properties are controlled to large extent by the efficiency of bonding at the fiber-matrix interface boundary. Besides, good adhesion at the interface could facilitate stress transfer from fiber to fiber across matrix and hydrophilic properties of natural fibers versus hydrophobic properties of plastics.

Surface modification has two methods which is chemical and physical treatment. The chemical modifications do not affect the body of the fiber and do not alter its structure. Only the outer surface of the grafted natural fibers obtained using this process is modified.

1.2 Problem Statement

In recent years, composites made of natural fibers have received increasing attention in light of the growing environmental awareness because of its biodegradable nature. However, the problems by using natural fiber which is kenaf bast fiber are lack of good adhesion between kenaf fiber and polymer matrices and low resistance to the moisture due to the surface impurities and hydrophilic nature of the fibers. These problems make the used of natural fiber as reinforcement material in composite become 'gloomy'.

1.3 Research Objectives

The objective of this research is to remove surface impurities such as lignin and hemicelluloses in order to make kenaf bast fiber more hydrophobic by using alkali treatment in order to produce high strength of thermoset compoite.

1.4 Scopes of Study

The scopes of this research were

- a) Preparation of the kenaf fiber
- b) Treatment conditions of kenaf fiber
- c) Characterization of treated kenaf fiber
- d) Composite fabrication method
- e) Characterization of thermoset composite produced.

1.5 Significant of Study

This study is conducted to investigate the effects of chemical modification on kenaf bast fiber by using NaOH solution. Alkali treatment is one of the methods to modified fibers surface in order to improve their characteristics as reinforcement in making the composite. This treatment will make the use of natural fiber like kenaf more attractive and effective in their many applications. Natural fiber also is economically and environmental friendly because of its biodegradable nature.

1.6 Expected Results

The elimination of amorphous non-cellulosic constituents (lignin and hemicelluloses) will increase the crystallinity, molecular alignment of cellulose, surface roughness of the fiber. Alkali treatment also can make fiber more hydrophobic in order to get good interfacial adhesion between fiber and thermoset polymer matrix.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter includes the literature review on the chemical modification and characterization of the kenaf fiber and the production of thermoset composite. The non-cellulose constituents on the kenaf fiber surface such as lignin and hemicellulose will lead to the production of low-quality of thermoset composite when this kind of fiber is combined to the thermosetting materials. Alkali treatment, by using sodium hydroxide will clean the surface of the fiber and enhanced performance of the thermoset composite.

2.2 Types of Fiber

Fibers or fibers are a class of hair-like materials that are continuous filaments or are in discrete elongated pieces, similar to pieces of thread (Wikipedia, 2010). They can be spun into filaments, thread or rope. They can be used as a component of

composite materials. Fiber can be classified into two main groups, which are man-made fiber and natural fiber. In general, natural fibers can be subdivided as to their origin such as plants, animals, or minerals; while man-made fibers can be subdivided to synthetic and natural polymers (Muhammad, 2008).

2.2.1 Natural Fibers

Natural plant and animal fibers have provided the raw materials to meet our fiber needs. No matter which climatic zone humans settled they were able to utilize the fibers of native species to make products such as clothes, cloths, buildings and cordage. The first composite material known was made with clay and straw to build walls in Egypt 3,000 years ago. Many of the ancient plant fibers are no longer in use. Fibers such as jute, sisal, coir and kapok only started to be imported into Europe from the nineteenth century (History of Natural Fiber, 2010).

The use of natural fiber for the reinforcement of the composites has received increasing attention both by the academic sector and the industry (Taj, Munawar, & Khan, 2007). Natural fibers (Amar, Manjusri, and Lawrence, 2005) are generally lignocellulosic in nature, consisting of helically wound cellulose microfibrils in a matrix of lignin and hemicellulose. Currently, many types of natural fibers have been investigated for use in plastics including flax, hemp, jute straw, wood, rice husk, wheat, barley, oats, rye, cane (sugar and bamboo), grass, reeds, kenaf, ramie, oil palm empty fruit bunch, sisal, coir, water, hyacinth, pennywort, kapok, paper mulberry, raphia, banana fiber, pineapple leaf fiber and papyrus (Bledzki et al., 2007).

2.2.2 Synthetic Fiber

Synthetic fibers are the result of extensive research by scientists to improve upon naturally occurring animal and plant fibers. In general, synthetic fibers are created by forcing, usually through extrusion, fiber forming materials through holes (called spinnerets) into the air, forming a thread. Before synthetic fibers were developed, artificially manufactured fibers were made from cellulose, which comes from plants. These fibers are called cellulose fibers. The first artificial fiber, known as artificial silk, became known as viscose around 1894, and finally rayon in 1924 (Wikipedia, 2010).

A similar product known as cellulose acetate was discovered in 1865. Rayon and acetate are both artificial fibers, but not truly synthetic, being made from wood. Nylon, the first synthetic fiber, made its debut in the United States as a replacement for silk, just in time for World War II rationing. Its novel use as a material for women's stockings overshadowed more practical uses, such as a replacement for the silk in parachutes and other military uses (Wikipedia, 2010). Synthetic fibers are now available, ranging in properties from the high elongation and low-modulus elastomeric fibers, through the medium-elongation and medium-modulus fibers such as polyamides and polyesters, to the low-elongation, high modulus carbon, aramid and inorganic fibers (Hannant, 1989; Jusoh, 2008). The modern synthetic fiber that was made from older artificial materials and became the most common of all reinforcing fibers for polymer matrix composites is glass fiber (Agarwal and Broutman, 1990; Jusoh, 2008).

2.3 Main Component of Natural Fibers

Fiber is actually very complex. It is a combination of at least four major components which are distinctly different in chemical composition. These four major components are cellulose, hemicellulose, lignin, and pectin.

2.3.1 Cellulose

Cellulose is the substance that makes up most of a plant's cell walls. Since it is made by all plants, it is probably the most abundant organic compound on Earth. Aside from being the primary building material for plants, cellulose has many other uses. According to how it is treated, cellulose can be used to make paper, film, explosives, and plastics, in addition to having many other industrial uses. The paper in this book contains cellulose, as do some of the clothes you are wearing. For humans, cellulose is also a major source of needed fiber in our diet (Science, 2010).

Cellulose is usually described by chemists and biologists as a complex carbohydrate. Carbohydrates are organic compounds made up of carbon, hydrogen, and oxygen that function as sources of energy for living things. Plants are able to make their own carbohydrates that they use for energy and to build their cell wall. Since cellulose is the main building material out of which plants are made, and plants are the primary or first link in what is known as the food chain (which describes the feeding relationships of all living things), cellulose is a very important substance. It was first isolated in 1834 by the French chemist Anselme Payen (1795–1871), who earlier had isolated the first enzyme. While studying different types of wood, Payen obtained a substance that he knew was not starch (glucose or sugar in its stored form), but which still could be broken down into its basic units of glucose just as starch can. He named this new substance "cellulose" because he had obtained it from the cell walls of plants (Science, 2010).

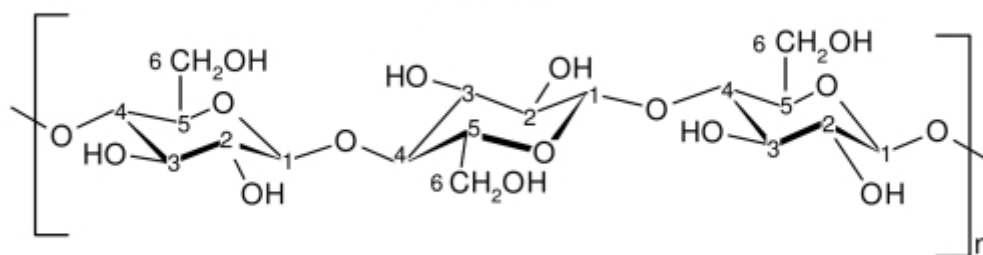


Figure 2.1: Cellulose structure (Cellulose, 2010)

Cellulose has a strong tendency to form intra- and inter-molecular hydrogen bonds by the hydroxyl groups on these linear cellulose chains, which stiffen the straight chain and promote aggregation into a crystalline structure and give cellulose a multitude of partially crystalline fiber structures and morphologies (Klemm, Heublein, Fink, and Bohn, 2005).

2.3.2 Hemicellulose

Hemicellulose is a polysaccharide composed of a variety of sugars including xylose, arabinose, mannose. Hemicellulose that is primarily xylose or arabinose are referred to as xyloglucans or arabinoglucans, respectively. Hemicellulose molecules are often branched. Like the pectic compounds, hemicellulose molecules are very hydrophilic. They become highly hydrated and form gels. Hemicellulose is abundant in primary walls but is also found in secondary walls (Plant Cell Walls, 2010).

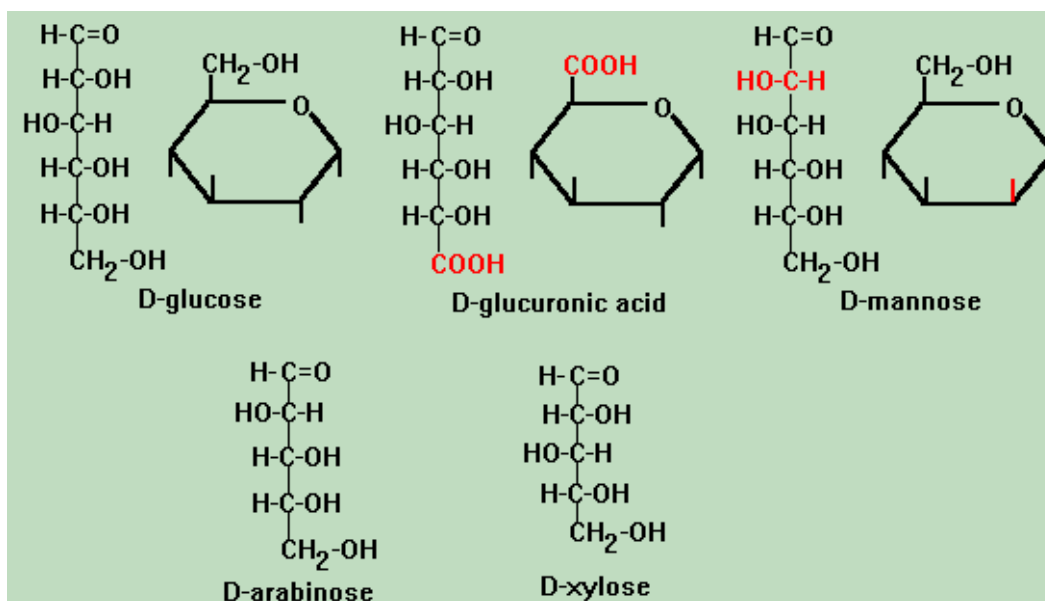


Figure 2.2: Some monomer of hemicelluloses (Hemicellulose, 2010).

Usually, all of the pentoses are present. There may even be small amounts of L- sugars. Note that there are hexoses as well as acids formed by oxidation of sugars. Mannose and mannuronic acid tend to be present, and there can be galactose and galacturonic acid. The groups that are different from glucose are shown in red on the six-carbon structures. The pentoses are also present in rings (not shown) that can be 5-membered or 6-membered. Xylose is always the sugar present in the largest amount (Hemicellulose, 2010).

In contrast to cellulose that is crystalline, strong, and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. It is easily hydrolyzed by dilute acid or base, but nature provides an arsenal of hemicellulase enzymes for its hydrolysis. These enzymes are commercially important because they open the structure of wood for easier bleaching, and older methods of bleaching consume larger amounts of chemicals such as chlorine that are bad for the environment (Hemicellulose, 2010).

2.3.3 Lignin

Lignin or lignen is a complex chemical compound most commonly derived from wood, and an integral part of the secondary cell walls of plants (Martone, Estevez, Lu, Ruel, Denny, Somerville, & Ralph, 2009; Wikipedia, 2010). The term was introduced in 1819 by de Candolle and is derived from the Latin word *lignum* (Sjöström, 1993).

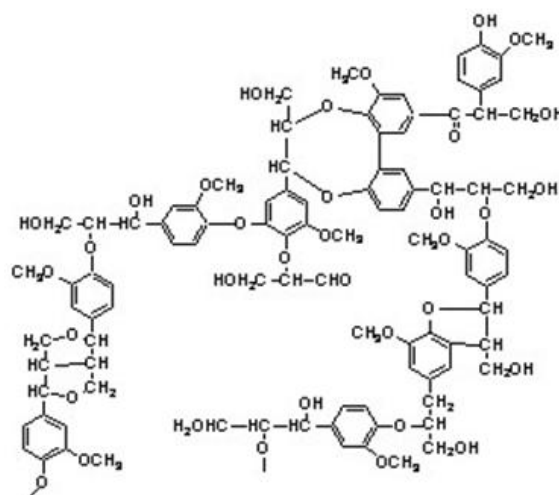


Figure 2.3: Structure of the lignin (Lignin, 2010).

Lignin can be classified in several ways but they are usually divided according to their structural elements. All plants lignin consist mainly of three basis building blocks of guaiacyl, syringyl, and p-hydroxyphenyl moieties, although other aromatic type units also exist in many different types of plants, which forms a randomized structure in a tri-dimensional network inside the cell walls (Xiao et al., 2001; James and Jeffrey, 1997; Jusoh, 2008). The function of the lignin in plants is as an encrusting agent in the cellulose/hemicelluloses matrix or called plant cell wall adhesive. Therefore, lignin acts as a structural support material in plants by filling the spaces between the polysaccharide fibers, which hold the natural structure of the

plant cell walls together (Sain and Panthapulakkal, 2004; James and Jeffrey, 1997; Jusoh, 2008).

2.4 Bast and Core Fiber

Bast fibers exist in the inner bark or phloem of many dicotyledonous plants to provide structural rigidity to the stems. These fibers occur in bundles which run parallel to the stems between nodes. The fiber strands are composed of many smaller cells termed ultimate fibers. Just inside the phloem is a wood-like core material consisting of short and fine fibers (Timothy and Michael, 1997; Jusoh, 2008).

According to Alexander et al. (2005), the shape and size of the stem of various bast fiber crops are different but they all contain varying amount of fiber cells in the phloem. Long individual fiber or long fibers bundles can be obtained from many bast fiber crops at relatively low cost. However, bast fibers have a non-homogeneous cell structure than do the much shorter wood fibers which are uniform, readily available and inexpensive (Jusoh, 2008).

Bast fibers have been used for generations to produce textiles and are removed from the phloem by a controlled decay and separation process called retting. In general, the core material is unused after the outer bast fibers are removed (Timothy and Michael, 1997; Jusoh, 2008). Bast fiber crops have rigid herbaceous stalks containing nodes at regular intervals that are fluted or channeled. From the inside to outside the stalks have a hollow core, except at joints, followed by the pith and finally the protective layer epidermis (Alexander et al., 2005; Jusoh, 2008).

2.5 Kenaf Bast Fiber

Kenaf, *Hibiscus Cannubinus* (Figure 1), is a plant from Malvaceae family. It is annual or biennial herbaceous plant (rarely a short-lived perennial) growing to 1.5-3.5 m tall with a woody base. The stems are 1-2 cm diameter, often but not always branched. Kenaf has a long history of cultivation for its fiber in India, Bangladesh, Thailand, parts of Africa, and to a small extent in southeast Europe. Kenaf fibers (Figure 2) have significant amount of amorphous lignin (15-19%) and amorphous hemicellulose (22-23%) along with crystalline cellulose (44-57%) (Sanadi & Caulfield, 2008). The fibers are made up of cellulose microfibrils bonded together by lignin. Hemicellulose is very hydrophilic, soluble in alkali, and easily hydrolyzed in acids while lignin is not hydrolyzed by acids, but soluble in hot alkali (John & Anandjiwala, 2009).

Kenaf fiber can be divided into two types: kenaf bast fiber and kenaf core fiber where kenaf bast fibers have thicker walls compared to the core fibers (Rowell and Stout, 2009). Kenaf bast fiber has high potential as a reinforcing fiber in thermoplastic composites because of its superior toughness and high aspect ratio in comparison with other fibers. The bast consists of a woody core surrounded by a stem. The stem consists of a number of fiber bundles, each containing individual fiber cells or filament like fibers (Rowell et al., 2009). Kenaf bast fiber is a composite made up of a crystalline, thermoset polymer matrix (lignin and the hemicellulose). Besides, kenaf, an annual hibiscus fiber plant, has been found to be an important source of fiber for composites and other industrial applications. A single fiber of kenaf can have a tensile strength and modulus as high as 11.9 GPa and 60 GPa respectively (Karnani, Krishnan, and Narayan, 2009). So, combining kenaf fiber with the thermoset material provides a strategy for producing advanced thermoset composite that take advantage of the properties of types of materials (Gaceva et al., 2009).



Figure 2.4: Kenaf plant (*Hibiscus Cannubinus*)



Figure 2.5: Kenaf bast fiber